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SILICATE-ZINC ANTIFOULING PAINTS

Studies on Antifouling Properties

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Studies on Antifouling Properties

by

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SILICATE-ZINC ANTIFOULING PAINTS
Studies on Antifouling Properties

From the results of investigations into the anticorrosion properties of antifouling silicate-zinc paints described in Part I, one may judge the best anticorrosion properties are those of coatings in which the external layer consists of antifouling paint containing 14.2 to 21.1% of Cu_2O (1). In the further course of the study the antifouling properties of these paints and compositions were studied.

For the compositions of antifouling paints a property quite as essential as anticorrosion action is biological action and the way it changes over time. The effectiveness of the antifouling action of copper oxide depends upon the speed with which the copper is washed out of the coating. The degree of washing out necessary for avoidance of fouling depends on the use conditions of the object being preserved. Under circumstances of severe fouling the indispensable minimum comes to about 10 μg Cu per square centimeter per 24 hours (2). Over the entire period of use of the paint the degree of washing out of copper from it cannot be less than this minimum.

With the purpose of characterizing the antifouling properties of coatings we used the accelerated tests which we had previously worked out, namely, determination of the toxicity of antifouling paints through photo-colorimetric identification of copper washed out in the form of a compound with glycine (3, 4, 5) and a laboratory method for pointing out curves of the washing out of copper (6). The results secured in the accelerated tests were compared with conditions at a marine station on land.

Experimental Part

of Coatings Investigated

Investigation of antifouling properties was carried out for silicate paints having a content of 14.2 to 90% of Cu_2O and 74.8 to 0% of zinc converted into dry mass terms. In the accelerated laboratory tests seven different coatings selected in a manner making possible comparison of antifouling properties of paints constituting the exterior layer of the coatings and the definition of the influence of the intermediate layer and of the base were tested. Tests at the land station were carried out for multiple-layer coatings in which the antifouling paints constituted the exterior layer laid down upon a base, or upon the base plus an intermediate layer. For comparison, test plates covered only with silicate-zinc paint without the addition of toxic substances, and also plates protected by a set of organic ship plates were investigated.

Method System for Laboratory Investigation

Glycine Test. Investigation was carried out by the method described in the literature (5) consisting of direct colorimetric examination of the copper-glycine complex created in the area of extraction of coatings in a solution of sodium glycinate. In the glycinate solution freeing of copper from the coating takes place about 100 times faster than in sea water, which makes it possible to secure essential data regarding the properties of a coating without need for prolonged exposure in sea water. In the course of 72 hours of extraction a quantity of copper close to the quantity washed out of the coating during the course of a year's exposure in sea water is liberated from the same unit surface of the coating (4).

Reagents and Apparatus. A water solution of sodium glycinate containing in 1 liter 28.8 cm^3 1 n NaOH, 1.785 grams of glycine, cz.d.a., and 28 grams of sodium chloride, (pH of a solution prepared in this way should come to 10.5). A Pulfrich Photometer, red filter having maximum absorption with $\lambda = 619 \text{ m}$. Lamp pH meter. Electromagnetic air pumps.

Carrying Out of Determination. Sand glass plates of $7.5 \times 10 \text{ cm}$ dimensions were covered on both sides with a paint or set of paints under investigation. The composition of the set included a silicate-zinc base, and intermediary

layer, and an antifouling paint, or the base and the antifouling paint. The painted surfaces were seasoned over four days at a temperature of about 20° C. The plates were placed in beakers containing 1 liter of the glycinate solution. Extraction was carried out over 72 hours at a temperature of 12 to 14° C, the solution being agitated by means of a stream of air secured from the electromagnetic pump. In a part of the solution the concentration of copper washed out was noted. Distilled water was used as a reference medium. The results were expressed in milligrams of Cu per square centimeter per 72 hours and are summarized in Table 1.

Table 1
Results of Glycine Test

a Rodzaj farby (powłoka zewnetrzna)	b Zawartość składników w przeliczeniu na suchą masę			c Ilość wymytej miedzi mg Cu/cm ² /72 h
	% Cu ₂ O	% Zn	d % siolwa	
F1	14,2	80	12	0,483
F3	21,1	57	12	0,486
F3*)	21,1	57	12	0,486
F3**)	21,1	57	12	0,495
F4	21,1	33,5	12	0,743
F7	45,0	28	20	1,410
F5	90,0	—	10	4,4

e *) Farba F3 naniesiona na podkład krzemianowo-cynkowy 7A

f *) Farba F3 naniesiona na podkład 7A i międzywarstwą M5 pigmentowaną czerwienią żelazową.

g) Pozostałe farby naniesione wprost na płytkę szklaną.

a) Class of paint (exterior coating); b) Content of Components expressed in terms of dry mass; c) Quantity of Copper washed out in milligrams of Copper per square centimeter per 72 hours; d) binder; e) %binder; e) #3 paint laid upon a silicate-zinc base 7A; f) # Figure 3 paint laid upon a 7A base and an intermediate layer of M5 pigmented with iron red; g) The remaining paints were laid directly on the glass plates.

Pointing Off of Curves for Washing Out of Copper

Curves for the washing out of copper were pointed off by the accelerated method described in literature (6) by making use of extraction in sodium glycinate.

The plates were exposed in the glycinate solution and the degree of washing out in artificial sea water after varying times of duration of the extraction in glycinates were set down. The copper washed out of the coating in

artificial sea water was determined by the colorimetric method of Callan and Henderson (7) in the form of a complex of sodium di-ethyl di-thio carbamate.

Reagents and Apparatus. Artificial sea water prepared by dissolving in 750 cubic centimeters of water 27 grams of NaCl, 17 milligrams of NaHCO_3 , and 3 milligrams of Na_2CO_3 and making up this with distilled water to a volume of 1000 cubic centimeters. The sodium glycinate solution was prepared as in the glycine test. Sodium di-ethyl di-thio carbamate C₂d.a. - 0.1%, in a solution of water. Citric acid cz. 50% water solution. Concentrated ammonia. Carbon tetrachloride cz.

Apparatus as in the glycine test, filter having maximum absorption with $\lambda = 465 \text{ m}\mu$, thermostat.

Carrying Out of Identifications. Painting on glass plates was done as in the glycine test. Extraction was carried out in the glycinate solution at a temperature of 16 to 18°C over a period of 8 to 16 hours. Next the plates were removed, washed off with distilled water and placed in beakers containing 1 liter of artificial sea water and lowered into the thermostat (Figure 1). After 1 to 2 hours of extraction - depending on the speed of washing - at a temperature of 25° C, plus or minus 1°, with constant agitation by means of a stream of air, the quantity of copper liberated from the coating was determined, and the plates were again placed in the glycinate. This cycle (extraction in glycinate, and then in artificial sea water) was repeated 7 times, the degree of washing out of copper being determined after each removal of the plate from the glycinate. The results are presented in Figures 3 and 5 in the form of so-called laboratory curves of washing out of copper.

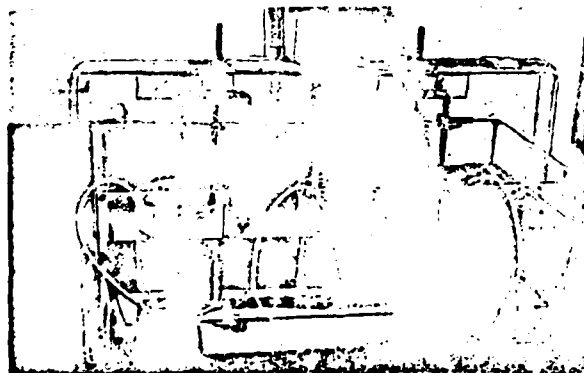


Figure 1
Apparatus for Extraction in Artificial Sea Water.

Land Investigations

Sanded steel plates of 25 x 50 centimeters dimension were twice coated with a 7A silicate-zinc base coat, then an intermediary coat was put on and two layers of anti-fouling paint. Specimens were also prepared without using the intermediary layer. In this case, two layers of anti-fouling paint were laid upon a plate covered twice with a 7A base. The paint covered plates were seasoned for 7 days, submerged in the basin of the fishing port of Wladyslawowo to a depth of 2.5 meters. The land station in Wladyslawowo belongs to an open, cold water milieu having an average annual temperature of 9.10 C and 7.62% salt. Fifteen-month period of exposition covered two periods of intensive growth of fouling, during which it was principally the barnacles *Balanus improvisus* that developed upon the specimen plates. The results of the 15-month exposition are presented in Table 2.

Table 2

Results of observation of fouling and corrosion of plates after 15 months exposition at the land station at Wladyslawowo *

a Rodzaj farby zewnętrznej	b Pąkle	c Szlam	d Algi	e Omul-ki	f Mszy-wioły	g Koroz-ja pod-łoża	h Uwagi
F2	1	2	2	2	2	2	
F3	1	2	2	2	2	4,3	
F4	4,5	2	2	2	2	4,3	j
F7	—	—	—	—	—	2	po 5 mies.
F5	4,5	2	2	2	2	2	
7A **)	1	2	2	2	2	4	
F3 **)	1	2	2	2	2	2	j
F3 **)	—	—	—	—	—	1	po 5 mies.
Farba orga-niczna 13/43/117	4	2	2	2	2	2	
1							

k*) Przyjęto następujący system oceny korozji i porostania

l 5 — brak zmian

m 4 — zmiany obejmujące poniżej 1% powierzchni

n 3 — zmiany powyżej 1—5% powierzchni

o 2 — zmiany powyżej 5—10% powierzchni

p 1 — zmiany powyżej 10—15% powierzchni

q**) Powłoki bez międzywarstw

a) Class of exterior paint; b) Barnacles; c) Slime; d) Algae; e) Mussels; f) Bryozoans; g) Corrosion of ground; h) Notes; i) Organic paint 13/43/117; j) After 5 months; k) The following system of evaluation of corrosion and fouling was applied; l) 5-absence of changes; m) 4-changes affecting less than 1% of surface; n) 3-changes between 1 & 5% of surface; o) 2-changes between 5 & 10% of surface; p) 1-changes about 10-15% of surface; q) **) Coatings without intermediary layer.

Discussion of Results

Results of Accelerated Tests

Glycine Test. Under the biologic conditions of the Baltic Sea, in order to secure effective action of anti-fouling coatings the quantity of copper washed out during the period of the test must come, for organic paints, to at least 0.6 milligrams of Cu per square centimeter per 72 hours (making allowance for the temperature of the determination) (5).

Among the silicate paints examined, this minimum was reached by the paints F4, F5 and F7 containing respectively 21.1%, 45%; and 90% of Cu_2O and 33.5%; 0%; and 28% of zinc in dry mass. Coatings of these paints during the period of duration of the test were subject either to total or to partial disintegration. For coatings of paints F2 and F3 containing 14.1 and 21.1% of Cu_2O and 60 and 57% of zinc the degree of washing away is somewhat lower than the required minimum. The results of the tests are set forth in Table 1.

Determination of Curves for Washing Away of Copper. As becomes apparent from the data presented in Figures 2 and 3, the copper of paints F4, F5, and F7 is washed out unevenly. The degree of washing out of the copper from coatings of paints F4 and F5 reaches very high values in a short time (2800 milligrams of copper per square centimeter per 24 hours for F4 after 24 hours) as a result of which destruction of the coating occurs.

For paints F2 and F3 containing a greater quantity of zinc dust and a lower quantity of toxic substances than the other paints, the curves for washing out of copper have an approximate course. The degree of washing out, R, exceeds the required minimum of 10 μg Cu per square centimeter per 24 hours (6) after 20 to 30 hours of extraction in glycinate, and comes approximately to the level of 20 to 40 μg of copper per square centimeter per 24 hours. The silicate-zinc base layer directly beneath the layer of antifouling paint F3 brings it about that the degree of washing out of copper fell at a somewhat lower level and intermediary layer pigmented with iron red leads to a rise in the speed of washing out (Figure 4).

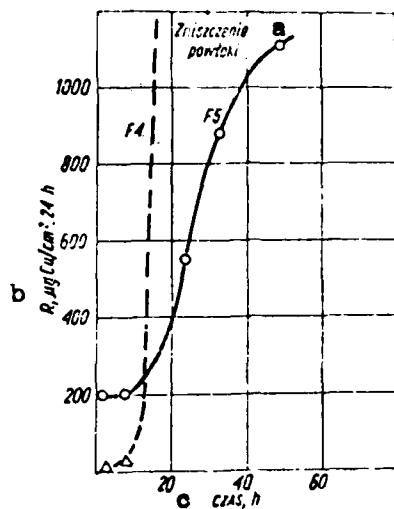


Figure 2

Curves for speed of washing out of copper R in relation to time of extraction in glycinate of coatings of paints F4 and F5.

a) Destruction of coating; b) R, μg of copper per sq. centimeter per 24 hours; c) Time in hours.

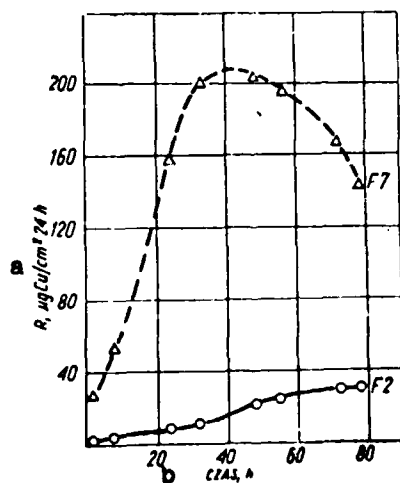


Figure 3

Curves for speed of washing out of copper R in relation to extraction time in glycinate of coatings made of paints F2 and F7.

a) R, μg of copper per sq. centimeter per 24 hours; b) Time in hours.

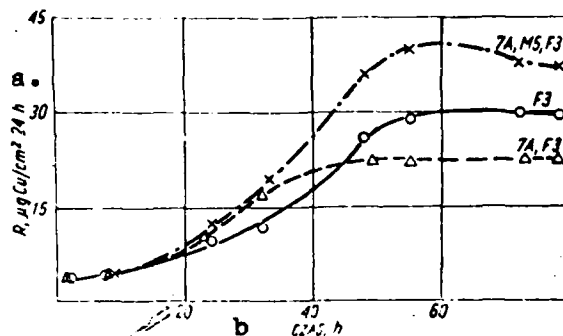


Figure 4

Curves for speed of washing out of copper R in relation to extraction period in glycinate for coatings of F3 paint laid directly upon glass plates, upon a 7A base, and upon an M5 intermediary layer plate.

a) R, μg of copper per sq. centimeter per 24 hours; b) Time in hours.

Results of Land Tests. During the first investigation period comprising the months of July, August and September, on plates painted with F7 paint and organic paint, small quantities of slime appeared. After 10 months of exposition the plates continued to be devoid of barnacles, but as they became covered with slime and green plant growth palpable differences set in, which were maintained over a further five months despite periodic washing off of the slime by means of a strong jet of water. After 15 months exposition, subsequent to a second period of intense fouling, it was determined that there was a large quantity of barnacles on plates covered only with silicate-zinc paint 7A and on plates painted with silicate antifouling paint F2 and F3. F3 paint containing 21.1% of Cu_2O counteracts fouling to a varying degree, depending on whether the paint was laid directly upon the silicate-zinc base, or instead, upon an intermediary layer. The use of an intermediary layer improves the action of the antifouling paint (Table 2 positions 2 and 7, 5 and 8) which is in agreement with the results of the accelerated tests (Table 1 positions 2,4; Figure 4).

A greater degree of overgrowth was determined to exist on plates having F2 paint.

Coatings of paints F4 and F5 laid upon a base plus an intermediary layer were distinguished by good antifouling properties. On plates having F4 paint a few barnacles appeared only in places where the exterior layer of the coating had flaked off. The remaining coatings of silicate paints were eliminated from the tests after 5 months by reason of the severe corrosion of their bases.

On all plates exposed for a period of 15 months we observed partial disintegration of the layer of antifouling plate. A coating of organic paints exposed over the same period exhibited a degree of coverage with barnacles, marine plants, and slime somewhat greater than that of the coating of silicate paints F4, F5, and in addition wrinkling and blistering had set in.

Conclusions

From the accelerated and land tests carried out it proves to be the case that the action of preservative coatings made of silicate paints depends in the main upon the content of copper oxide in the antifouling paint constituting the exterior layer of the coating. With increase in the content of Cu_2O anticorrosion properties became worse and antifouling properties became better. Thus, for example, a paint containing 90% Cu_2O has good antifouling properties, but the anticorrosion resistance is insufficient.

Coatings made of paints having a content of 21.1% of Cu_2O are distinguished by good anticorrosion properties, but their resistance to fouling, primarily on the part of barnacles, is insufficient.

The use of an intermediary layer pigmented with iron red advantageously affects the preservation of the base and hastens the washing away of copper.

Improvement of the anticorrosion and antifouling properties is insured by introduction into a paint having a fairly low copper oxide content, of zinc oxide, which improves the antifouling action of the coating without negative influence on anticorrosion properties. Optimum properties were shown by F4 paint containing 21.1% Cu_2O and 33.5% Zn, converted into dry mass terms, and also by zinc white laid down upon a silicate-zinc base plus an intermediary layer. Such a combination insures practically complete defense against corrosion and fouling over a period of at least 15 months. Over

such a period as this, fouling under the biological conditions of the Baltic Sea is limited to individual barnacles appearing in places where there has been major damage to the coating and to minor quantities of slime and feebly developed marine plants. The combination of organic paints examined under the same conditions protects the steel base both against corrosion and against fouling to a markedly less effective extent.

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